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Energy Procedia 146 (2018) 92–102

Energy Procedia

www.elsevier.com/locate/procedia

International Carbon Conference 2018, ICC 2018, 10–14 September 2018, Reykjavik, Iceland

In situ carbon mineralization in ultramafic rocks: Natural processes and possible engineered methods

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Abstract

In this invited review, we summarize the main results of ongoing research on "*in situ*" carbon mineralization in ultramafic rocks, including outcrop studies in Oman (e.g., [1, 2]), investigation of carbon mass transfer in subduction zones from the Oman Drilling Project (e.g., [3-7]), laboratory investigations (e.g., [8-12]) and numerical modeling (e.g., [13-17]) of the pressure of crystallization and reaction-driven cracking, and assessment of the rate, cost and capacity of various proposed methods for engineered carbon mineralization [18, 19].

Selection and peer-review under responsibility of the publication committee of the International Carbon Conference 2018.

Keywords: Mantle peridotite; reaction-driven cracking; pressure of crystallization; carbon capture and storage; CO_2 removal from air

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Selection and peer-review under responsibility of the publication committee of the International Carbon Conference 2018.
10.1016/j.egypro.2018.07.013

1. Introduction

Natural carbon mineralization in ultramafic rocks, particularly in tectonically exposed mantle peridotites, provides striking field evidence for rapid and complete uptake of CO_2 from the atmosphere and natural fluids to form solid carbonate minerals. Such processes – particularly in the oceanic upper mantle near oceanic spreading ridges, the outer rise near deep sea trenches, and in the "leading edge of the mantle wedges" overlying subduction zones – form important reservoirs in the global carbon cycle (e.g., [20]). Formation of weak layers of carbonate minerals, and related, hydrous Mg-silicates such as serpentine, is important in creating and maintaining tectonic plate boundaries. Oxidation and reduction of dissolved carbon species during peridotite alteration may lead to abiotic synthesis of hydrocarbons, and provide an energy source for subsurface, chemosynthetic microbial communities.

Seifritz [21] and Lackner et al. [22] proposed that spontaneous, exothermic, rapid carbon mineralization in peridotite could be harnessed for CO_2 capture and storage. This idea gained credence with experimental confirmation that olivine undergoes carbonation (via Mg_2SiO_4 olivine + 2 CO_2 = 2 $MgCO_3$ magnesite + SiO_2 quartz) faster than any other abundant, rock-forming mineral [19, 23-25]. Proposed engineered methods may be divided into *ex situ* processes – quarrying and grinding rock reactants, and transporting them to pressure vessels, where they react with fluid at high temperature and a high partial pressure of CO_2 – and in situ processes, in which CO_2 is transported by fluid flow along fractures and pores into subsurface rock formations at naturally elevated temperature and pressure. In this paper, we also refer to natural, subsurface carbon mineralization as an *in situ* process.

Nomenclature

Ultramafic	rock containing <45 wt% SiO_2 and >18 wt% MgO, and/or composed of >90 wt% "mafic minerals", which are olivine, pyroxenes, amphiboles, and serpentines
Peridotite	ultramafic rock containing more than 40% olivine (aka "peridot")
Olivine	mineral solid solution between end-members forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4); olivine comprises more than 60% of the Earth's upper mantle, where it is ~ 90% forsterite
Serpentine	hydrous silicate mineral group with Mg-end member $Mg_3Si_2O_5(OH)_4$; formation of serpentine plus other minerals by hydration of ultramafic rocks is often called *serpentinization*; rocks composed mainly of serpentine are called *serpentinites*
Carbonates	minerals such as *magnesite* ($MgCO_3$), *calcite* ($CaCO_3$) and *dolomite* ($MgCa(CO_3)_2$); formation of carbonate minerals by reaction of CO_2 with Mg- and Ca-bearing silicates is commonly called *carbonation* and *carbon mineralization*
Listvenite	rock composed of carbonate minerals + quartz + Fe-oxides + Cr-rich oxides or silicates, produced by complete carbonation of peridotite, in which all Mg and Ca combine with CO_2, most Fe forms oxides, and all SiO_2 forms quartz
Quartz	SiO_2 mineral
Crust	Relatively low density, SiO_2-rich, uppermost layer of the solid Earth; oceanic crust is about 7 km thick; continental crustal thickness is variable but averages ~ 36 km
Mantle	Relatively dense, ultramafic layer of the solid Earth, underlying the crust; the upper mantle – from the base of the crust to ~ 410 km depth – is composed of peridotite and contains abundant Mg-rich olivine
Spreading ridge	narrow zone of extension and formation of new, igneous ocean crust between two diverging tectonic plates
Subduction zone	thrust fault at zone of convergence between two tectonic plates where one plate is thrust beneath the other; typically, old oceanic crust is thrust into the mantle
Hanging wall	block of rock overlying an inclined fault plane
Mantle wedge	mantle portion of the hanging wall above a subduction zone
Ophiolite	fragment of oceanic crust and upper mantle – an oceanic plate – thrust onto a continental margin

2. Outcrop studies

Outcrop studies of partially to fully carbonated peridotite provide a range of data; field relationships, whole rock geochemistry, mineral assemblages and compositions, and thermodynamic modeling – that support the hypotheses that these processes are geologically rapid, lead to reduction and oxidation of dissolved carbon species, and involve addition of substantial CO_2 (± H_2O) to form solid hydrates and carbonates, decreasing the solid density, combined with removal of comparatively small amounts of other, dissolved components (review [26]; more recent work, e.g., [27-49]). Peridotite carbonation and hydration (serpentinization) thus causes substantial increases in solid mass and volume. Such changes could lead to negative feedbacks – clogging porosity and armoring reactive surface area – but geologic examples of complete carbonation and serpentinization indicate that these feedbacks do not always limit the extent of reaction. The supply of CO_2 to reactive mineral surfaces via fluid flow along new fractures, which form during peridotite alteration, clearly plays a major role in the carbon mineralization process. Carbonate minerals in altered peridotite commonly form veins in fractures. Textures record coeval carbonate deposition and expansion of the rock volume. In fully carbonated peridotites (listvenites), quartz as well as carbonate veins are present, vein densities are high, and the rock matrix between veins is 100% carbonate + quartz + Fe-oxides + minor Cr-bearing minerals.

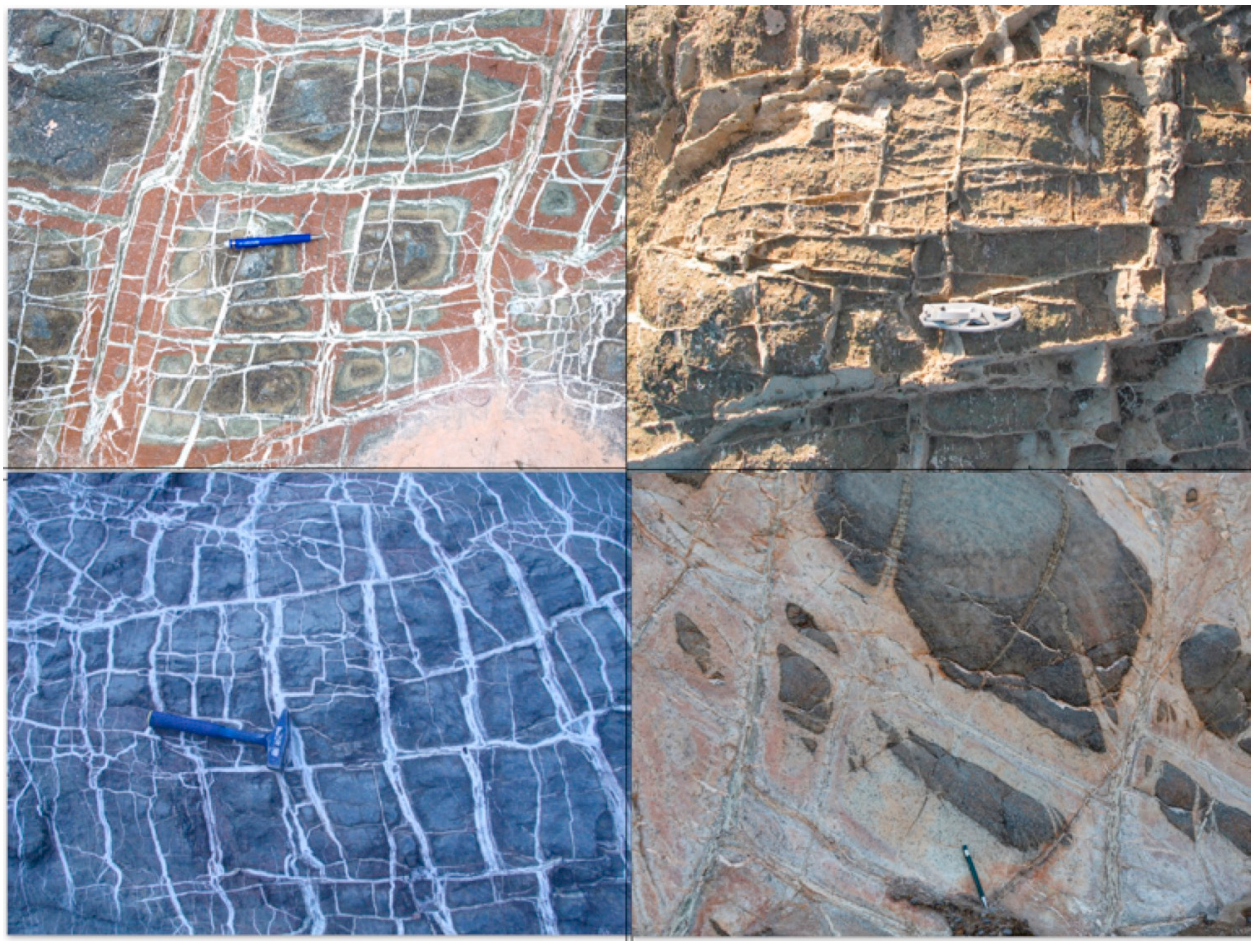

Fig. 1. White carbonate veins in partially serpentinized peridotites in Oman. Two left hand images: Kelemen pers. comm. 2017; top right: Kelemen and Matter [51]; bottom right: Falk and Kelemen [31].

3. Carbon mass transfer in subduction zones

Fully carbonated peridotites (listvenites) are exposed along the basal thrusts of some ophiolites, including the Samail ophiolite, which is a block of oceanic crust and upper mantle in Oman and the UAE that was emplaced along the Arabian continental margin about 70 million years ago [50]. For 25 million years prior to emplacement, the Samail ophiolite formed the hanging wall above a subduction zone, beneath which several hundred kilometers of oceanic crust and deep sea sediment were thrust into the mantle. Studies of the listvenites showed that they formed at ~100 °C, by carbonation of the shallow, "leading edge of the mantle wedge", with CO_2 supplied by fluids generated from decarbonation of the underlying, subducting sediments [31]. In 2017, Hole BT1B of the Oman Drilling Project sampled 200 meters of listvenite and serpentinite, the basal thrust fault (former subduction zone), and 100 meters of underlying metamorphosed sediments. Preliminary results from core analysis include evidence for generation of CO_2-bearing aqueous fluids from subducting sediments at higher temperature and pressure, followed by unmixing of the ascending, cooling fluid into H_2O-rich and CO_2-rich, immiscible components that formed different mineral assemblages within the listvenites [3-7]. In the context of potential, engineered in situ carbon mineralization, the primary relevance of these results is that 100% peridotite carbonation can be achieved at moderate temperatures and CO_2 partial pressures.

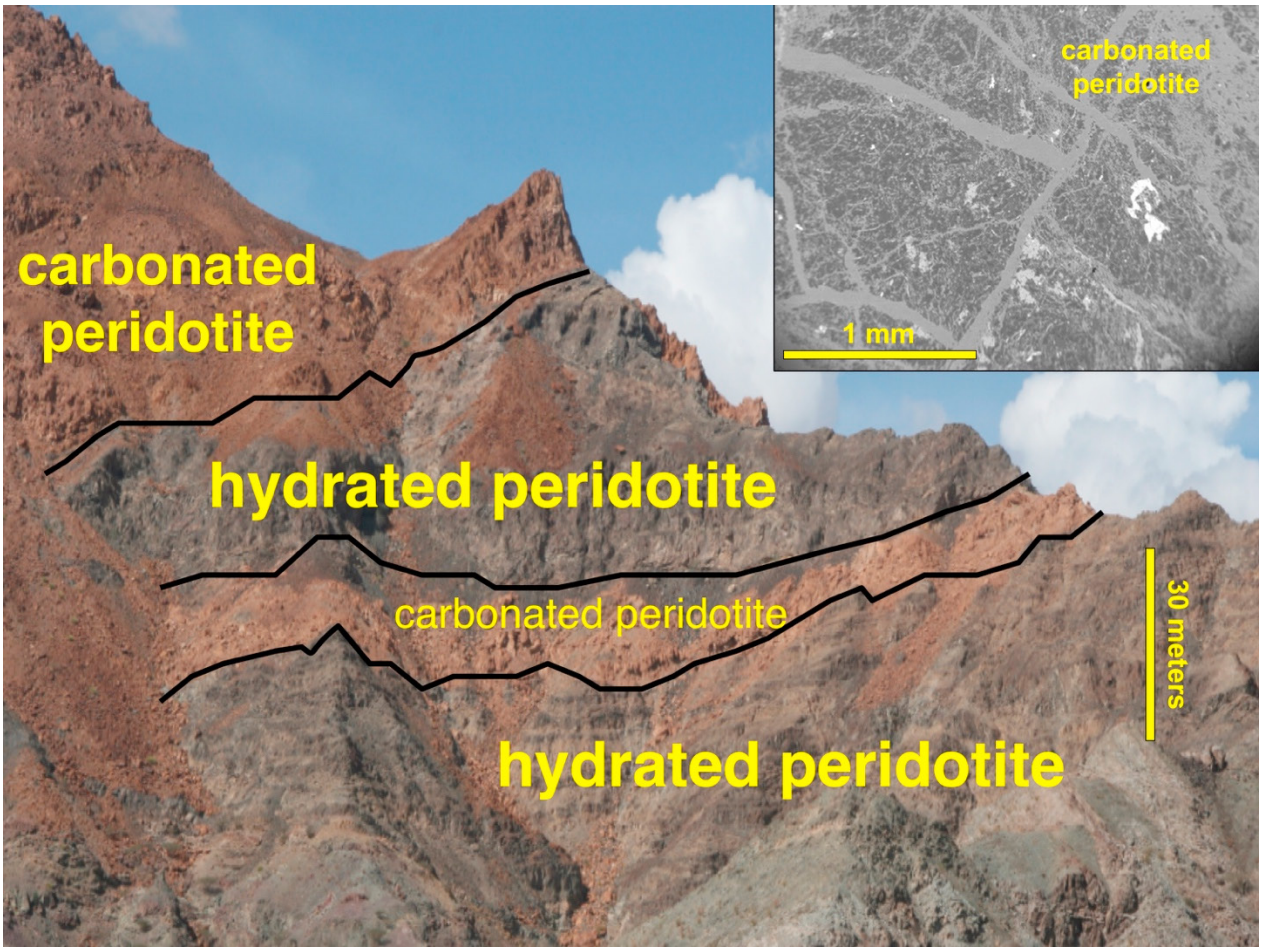

Fig. 2. Red bands of fully carbonated peridotite (listvenite) in green-grey partially serpentinized mantle peridotite in Oman. Inset is a back-scattered electron image of listvenite, in which dark grey areas are magnetite ($MgCO_3$), light grey areas are quartz (SiO_2) and bright grey and white areas are Cr-rich oxide minerals. Modified from Falk and Kelemen [31].

4. Laboratory and theoretical investigations of the pressure of crystallization and reaction-driven cracking

Kelemen and Matter [51], Rudge et al. [52], Kelemen et al. [26], Kelemen and Hirth [53] and Evans et al. [17] proposed that large increases in the solid volume during peridotite serpentinization and carbonation might lead to "reaction-driven cracking" (aka reactive cracking). Volume increases within an elastic container produce stress, known as the pressure of crystallization, which can lead to fracture formation, in a positive feedback mechanism that maintains or enhances permeability, fluid flow, and reactive surface area. We pointed to previous and concurrent work on cracking caused by serpentinization [15, 16, 54-57], by "salt weathering" (reviews in [58-60]), and by reaction-driven cracking in general (e.g., [61-63]). The overall concept seems simple enough, and reaction-driven cracking has been observed in peridotite carbonation experiments [64], as well as analog experiments on hydration of periclase (MgO) to produce brucite ($Mg(OH)_2$) [12]. Other analog experiments have demonstrated that significant crystallization pressures are generated by hydration of lime (CaO) to form portlandite ($Ca(OH)_2$) (up to 153 MPa, [8, 11]) and of basanite ($CaSO_4$•½ H_2O) to produce gypsum ($CaSO_4$•$2H_2O$) [9]. In the latter case crystallization pressure is limited due to stress relaxation via viscous creep of weak gypsum. Similarly, frictional yielding of brucite at ~ 30 MPa [65-67] may limit the maximum stress in the experiments of Zheng et al. [12].

In other experimental tests of olivine carbonation and hydration, volume change and fractures were not observed [10], and permeability dropped with increasing reaction progress [68-73]. The reasons for these varied experimental results are not yet clear. It is becoming apparent that micro- and nano-scale properties of fluid-rock systems, such as fluid-mineral surface energy, and related characteristics such as sorptivity and disjoining pressure [8, 12, 17, 58, 74, 75] may play a significant role in locating the crucial bifurcation between self-limiting negative feedbacks (clogging) and accelerating, positive feedbacks (cracking). Other processes, for example, selective, local dissolution and precipitation processes and/or crack propagation from etch pits along dislocation boundaries and other defects in olivine crystals [49, 72, 73, 76-82] – may also play a role in sustaining permeability and fluid flow. Perhaps, complete carbonation in natural systems is relatively slow, and thus cannot be engineered on a human time scale, as suggested by Van Noort et al. [10]. However, in the competition between (i) volume expansion and stress accumulation, and (ii) processes that relax elastic stresses such as pressure solution or frictional sliding along existing fractures, it seems likely that reaction-driven cracking happens when the rates of reaction and volume change are maximized.

This is an active and fertile topic for ongoing research. Understanding positive and negative feedbacks between reaction and fluid flow is crucial for any applied method of in situ carbon mineralization, particularly in peridotite formations with limited initial porosity.

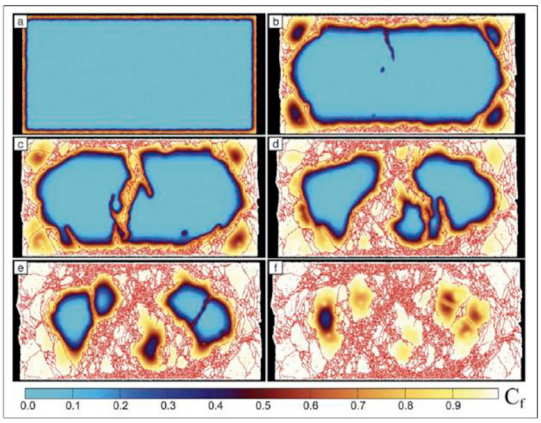

Fig. 3. Numerical model of reaction driven cracking from Royne et al. [13] in a rectangular block of rock surrounded by fluid in 2D. Blue rock reacts with surrounding black fluid to form white solid product, with volume increase and associated stress concentrations forming red cracks. In turn, red cracks provide rapid fluid access deeper into the block of rock. This discrete element model provides clear simulations of fracture formation at the grain scale, but does not incorporate Darcy flow within the porous fracture network.

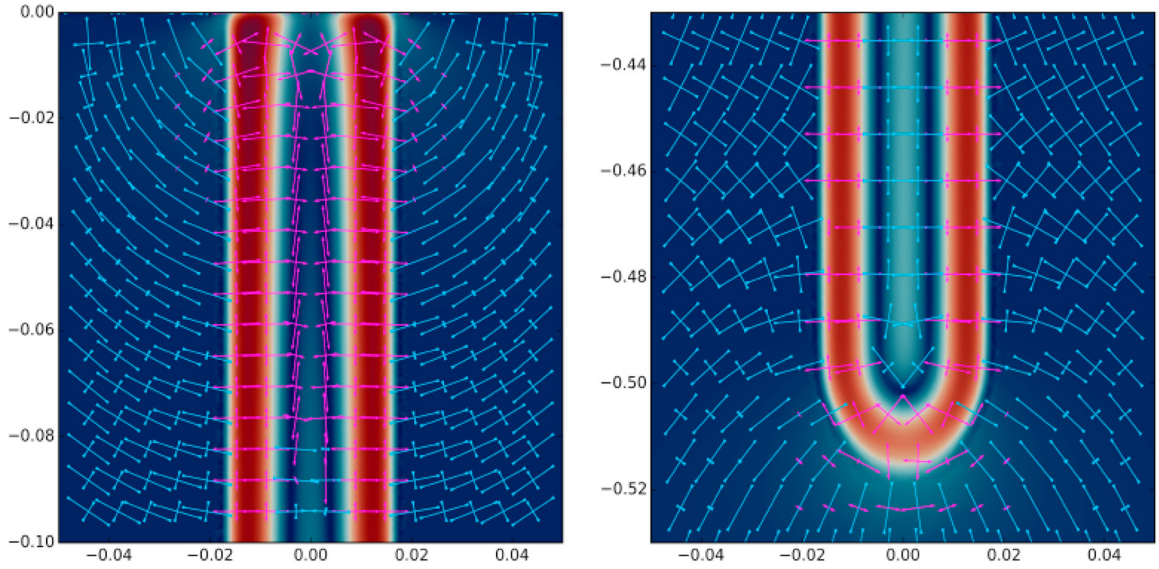

Fig. 4. From Evans et al. [17]. Non-dimensional stress magnitudes (colors) in 2D model of a tabular zone of high porosity infiltrated by CO_2-rich fluid, reacting with olivine to produce carbonate minerals with volume expansion. The pink and blue arrows indicate tensile and compressive stresses respectively. These stress orientations should result in horizontal fractures, perpendicular to the initial, vertical zone of high porosity.

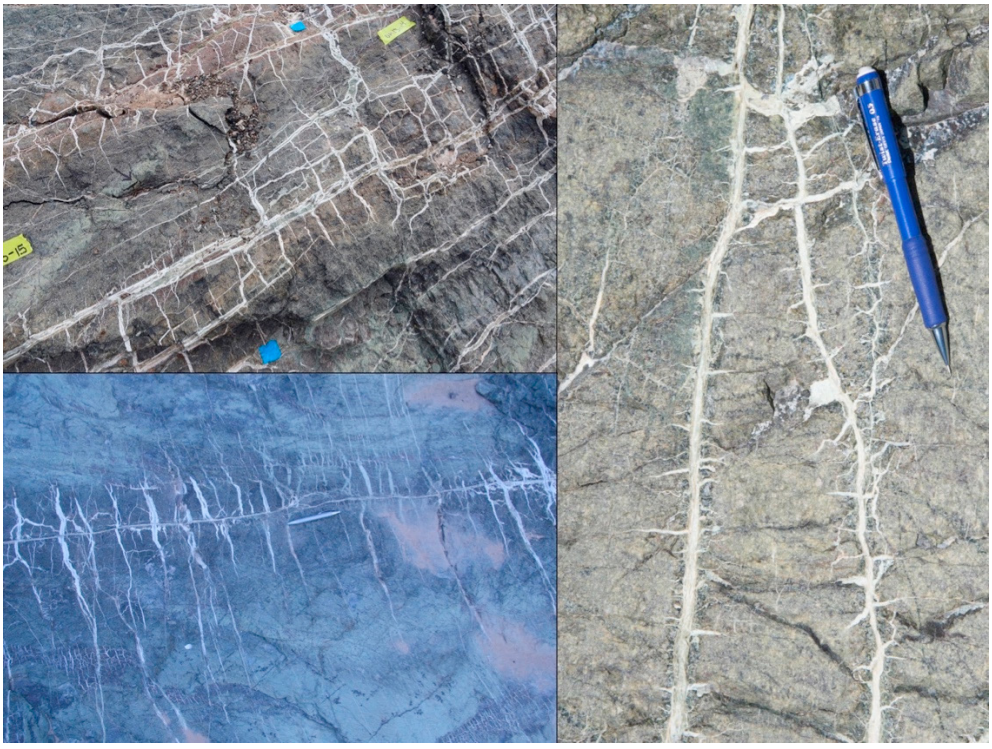

Fig. 5. From Evans et al [17]. White carbonate veins in partially serpentinized peridotite in, with the characteristic texture we call “ladder cracks” or “Frankenstein veins”. A central, carbonate vein is flanked by smaller, terminated, carbonate veins perpendicular to the central one.

5. Rate, cost and capacity of proposed methods for engineered carbon mineralization

Building upon our respective research programs, in response to requests by several groups reviewing methods for carbon dioxide removal from air (CDR), as well as associated CO_2 storage, a group of us (Aines, Benson, Dipple, Gadikota, Kelemen, Renforth, Wilcox) have compiled estimates of rates, reservoir capacities and costs of carbon mineralization in ultramafic rocks, in comparison with values for other proposed methods of CDR and CO_2 storage. We are now in the process of preparing papers on the results [18, 19]. These are not yet complete, and are the product of extensive literature review, so with apologies we will refrain from most citations, and limit the quantitative information shared here.

Some tentative highlights include: Mine tailings are the "low hanging fruit", and can achieve CDR at costs much lower than manufactured air capture systems, as recently reviewed by, e.g., [83]). There is significant industry interest in applying carbon mineralization, for CDR and/or storage of CO_2 captured from point sources, at the Mt. Keith mine (e.g., [84]) and more generally by the DeBeers diamond-mining consortium [85]. However, the CO_2 uptake capacity of mine tailings (existing, and produced annually) is low compared to human emissions of CO_2 and other greenhouse gases. Mining and processing ultramafic rocks for the purpose of CDR + solid storage may be cost and capacity competitive with manufactured air capture systems + storage, within the uncertainties of estimates for both options. However, at rates of Gt CO_2/yr, these methods might generate unacceptable volumes of tailings. Dispersal of finely ground olivine and/or brucite in agricultural soils, along shorelines, or in the shallow oceans, may also be similar in cost and capacity to manufactured CDR systems, but rates are so low, reactants are so dispersed, and areas are so large that this has been difficult to assess quantitatively.

CO_2 storage via *in situ* carbon mineralization in ultramafic rock formations may be cost and capacity competitive with storage of supercritical CO_2 fluid in subsurface pore space. However, this depends on avoiding negative feedbacks due to "clogging" of pore space and armoring of reactive surfaces as discussed in Section 4, above. Positive feedback regimes may exist, for example via "reaction-driven cracking" driven by stress due to solid volume change during carbonate crystallization. This is a topic for continued, basic research.

CDR via circulation of surface water through subsurface ultramafic rocks is less likely to generate clogging and passivation, compared to circulation of CO_2-rich fluids, but could be economically feasible only where the geothermal gradient and permeability are sufficiently high for thermal convection. This is because the CO_2 concentration in water saturated in air is ~ 100 ppm, so \$0.01 spent pumping a mass of water is equivalent to \$100 for the same mass of CO_2. Instead or in addition, combined CDR and geothermal power generation is possible in some regions.

While experiments on the rate of dissolution and/or carbon mineralization via reaction of aqueous fluids with various rock materials are fairly numerous, comparisons are hindered because different experimental conditions were used with different rock reactants. Gadikota et al. [18] performed a direct comparison of carbonation rates for olivine, plagioclase, basalt, and anorthosite (gabbro) with the same P, T, duration, and fluid composition, and similar grain sizes. These experiments confirmed that olivine undergoes more rapid carbonation than the other materials. Addition of $NaHCO_3$ increases carbonation rates for several of these materials (though in natural systems buffering of pH by water/rock reaction may have a similar effect). While most rock materials undergo passivation and decreasing reaction rates with increasing reaction progress, in most cases experimental olivine carbonation rates are approximately constant to more than 90% completion [18, 23, 25, 86]. This may be due to "reaction-driven cracking", formation of etch pits, and/or other processes that continually renew olivine reactive surface area.

6. Conclusion

Study of *in situ* carbon mineralization in ultramafic rocks is an active field of basic and applied research. Work to date has identified many essential processes that are not well understood, which can form the basis for highly rewarding, continued investigation. Engineered methods that emulate spontaneous, natural systems could – in principle – harness the chemical potential energy inherent in disequilibrium between the atmosphere and tectonically exposed rocks from the Earth's interior, thereby reducing cost and energy demands. However, such methods remain almost entirely speculative. A few small- to medium-scale pilot experiments, similar to the CarbFix and Wallula experiments on *in situ* carbon mineralization in basalt [87-96], would greatly advance knowledge and assessment of the feasibility of large-scale application of these ideas.

Acknowledgements

Our thanks to the organizers of the International Carbon Conference (ICC-2018).

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